

Towards New Oligomeric Spirobifluorene Derivatives:
Synthesis And Electrochemistry Of 2- And 2,2'-
Spirobifluorene Aldehydes.

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The importance of organic compounds bearing a spiro carbon in various fields of chemistry and material science is steadily increasing (1). The prediction (2) that *e.g.* a spirobifluorene derivative could be used in molecule-based computer hardware seems not far from being achieved (3). We have been interested in the syntheses and electrochemistry of such compounds since 1991 (4). Here we describe the preliminary results concerning aldehydes (1) and (2). Compounds (1) and (2) were prepared through a 1-step procedure starting from spirobifluorene (5). Cyclic Voltammetry (CV) and controlled potential reduction of aldehyde (1) (Figure 1 and Table 1) demonstrate the formation of its (green) radical anion. The 1-electron reduction is chemically irreversible (the corresponding anodic process is barely discernible). In fact, as expected (6) and confirmed by preparative electrolysis, a bimolecular process originates a red anionic intermediate. Acidic quenching and work-up furnish ultimately a main product, diol (4), (55 %), with substantial presence (10 %) of alcohol (3). 2,2'-dialdehyde (2) (CV results only are here reported), in strictly aprotic solvent (DMF, as above), gives the most interesting result, in that a radical anion is obtained in this case too. For the sake of comparison, an obvious choice is the biphenyl aldehyde (5); the corresponding pinacols are of limited solubility in the common solvents. To improve solubility of sparingly soluble molecules, bulky substituents are generally used. These are typically aliphatic and therefore may adversely influence some desirable electronic properties. Thus, an additional result reported here is that spiro shaped molecules may be a convenient alternative, as far as solubility problems are concerned.

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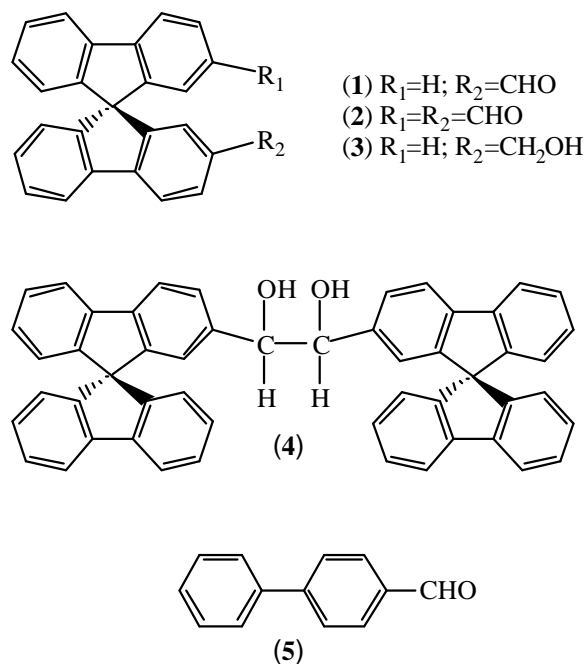


Table 1.

Compd	F/mol	dI ^a diol %	meso ^a diol %	alcohol ^a %	aldehyde ^a %
(1)	0.5	40	15	10	35
(5)	1.0	35	25	35	5

Controlled Potential Electrolysis data for compound (1) and (5). Solvent System: DMF-Et₄NClO₄ 0.1 M. Glassy carbon cathode. C(1)=1.0x10⁻³ M. C(5)=8.0x10⁻² M. E_{app}= -1.8 V vs. SCE. a) based on ¹H-NMR analysis of the mixture.

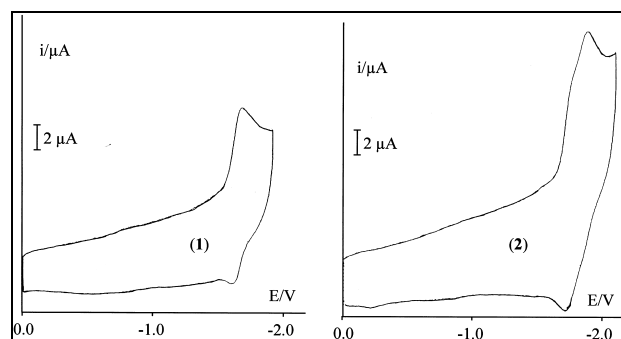


Figure 1.
Cyclic voltammograms of 2-formyl-9,9'-spirobifluorene

(**1**) and 2,2'-diformyl-9,9'-spirobifluorene (**2**).

Solvent System: DMF-Et₄NClO₄ 0.1 M. *E/V vs. SCE.*

Sweep rate $\nu=50\text{ mVs}^{-1}$. Glassy-carbon electrode.

C(**1**) = C(**2**) = 5.0×10^{-4} M.